PB84-185214

Air Pollution Effects on Aquatic Ecosystems
Summary of a Symposium

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Apr 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-185214

EPA-600/9-84-010
April 1984

Air Pollution Effects on Aquatic Ecosystems

Summary of a Symposium

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/9-84-010	2.
3. RECIPIENT'S ACCESSION NO. PB84 185214	
4. TITLE AND SUBTITLE Air Pollution Effects on Aquatic Ecosystems: Summary of a Symposium	5. REPORT DATE April 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R.W. Elias, T.B. Inge,* P. Von Ward*	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Health and Environmental Assessment Environmental Criteria and Assessment Office (MD-52) Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Office of Health and Environmental Assessment Office of Research and Development U.S. Environmental Protection Agency Washington, DC 20460	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA/600/21

15. SUPPLEMENTARY NOTES *Delphi Research Associates, 1346 Connecticut Ave., NW, Suite 310, Washington, DC 20036

16. ABSTRACT Summarizing presentations at a symposium on air pollutant effects on aquatic ecosystems, this document includes an overview of U.S. research programs, atmospheric emissions and deposition, cycling processes, and effects on plants and animals.

Current U.S. research addresses ecosystem classification and inventory by sensitivity to acidity, interactions between watershed terrestrial and aquatic ecosystems, and effects.

Atmospheric input to aquatic ecosystems may be gaseous or particulate and by wet and dry deposition. Particle dry deposition is most predictable; gaseous dry deposition models exist but are not yet reliable for regional scale. Linear correlation may exist between air sulfate content and deposition acidity. Source apportionment has been used to relate deposition to emission sources.

Radioactive isotope studies of cycling processes within aquatic ecosystems have shown that particulate metals are usually removed from the aqueous phase by sedimentation rather than with outflowing water. A chronological record of atmospheric inputs to aquatic ecosystems may be found in carefully taken sediment samples.

The earliest detectable effect of atmospheric pollutants on aquatic ecosystems is often change in species composition: for example, recently observed decline and disappearance of certain plant populations in acidified fresh water systems in The Netherlands. Fish and amphibians are also affected by lower pH.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 53
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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Preface

Panel 3 of the North Atlantic Treaty Organization Committee on the Challenges of Modern Society (NATO/CCMS) Pilot Study on Air Pollution Control Strategies and Impact Modeling conducted a two-day seminar in Chapel Hill, North Carolina, on the Impact of Pollutants on Aquatic Ecosystems. The seminar, chaired by Michael A. Berry, Chairman of Panel 3, Environmental Impact, consisted of eleven papers presented both by Americans and Europeans on the following subtopics: aquatic ecosystem research programs, the mechanisms of atmospheric emissions and deposition, the cycling processes within aquatic ecosystems, and effects of atmospheric pollutants on aquatic ecosystems.

The report which follows is the U.S. contribution to the panel's report. It is divided into two parts. Part I, prepared by Dr. Robert Elias, Environmental Criteria and Assessment Office, U.S. Environmental Protection Agency, presents an overview of the seminar and a summary of its conclusions. Part II, prepared by the staff of Delphi Research Associates, Washington, D.C., summarizes the American and European presentations made during the two-day seminar, though Dr. Elias provided the summary of Dr. Gary Glass's presentation on the hydrological cycle. The NATO/CCMS panel report will consist of these presentations together with member nations' overview reports.

Abstract

This document summarizes presentations at a symposium on air pollutant effects on aquatic ecosystems. These include an overview of U.S. research programs, atmospheric emissions and deposition, cycling processes, and effects on plants and animals.

Current U.S. research addresses ecosystem classification and inventory by sensitivity to acidity, interactions between watershed terrestrial and aquatic ecosystems, and effects. Experimental programs must often be longer than 2-3 years, as aquatic ecosystems are cyclic and successional.

Atmospheric input to aquatic ecosystems may be gaseous or particulate and by wet and dry deposition. Particle dry deposition is most predictable; gaseous dry deposition models exist but are not yet reliable for regional scale. There appears to be linear correlation between air sulfate content and deposition acidity. Source apportionment has been used to relate deposition to emission sources.

Radioactive isotope studies of cycling processes within aquatic ecosystems have shown that particulate metals are usually removed from the aqueous phase by sedimentation rather than with outflowing water. A chronological record of atmospheric inputs to aquatic ecosystems may be found in carefully taken sediment samples.

The earliest detectable effect of atmospheric pollutants on aquatic ecosystems is often change in species composition: for example, recently observed decline and disappearance of certain plant populations in acidified fresh water systems in The Netherlands. Fish and amphibians are also affected by lower pH.

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I. INTRODUCTION

This report on the impact of selected air pollutants on aquatic ecosystems is the United States' contribution to the third of four planned documents of Panel 3, Environmental Impact, of the NATO/CCMS pilot study on Air Pollution Control Strategies and Impact Modeling.

The Committee on the Challenges of Modern Society (CCMS) of the North Atlantic Treaty Organization (NATO) was created by the North Atlantic Alliance in 1969 to assist member states in the exchange of technical research and in cooperative projects on common problems. The principal mechanism for accomplishing these objectives is the multi-national pilot study. Fourteen pilot studies are under way in a variety of fields; eight are in the follow-up phase and thirteen have been completed.

NATO/CCMS has been particularly effective in the field of air pollution. One of the first efforts of the Committee was the Air Pollution Pilot Study led by the United States and co-piloted by Germany and Turkey. A second successful pilot study, Air Pollution Assessment Methodology and Modelling, now in its follow-up phase, was led by Germany, with Belgium and the United States serving as co-pilots. The current study is not a second or third phase of the preceding efforts, but it is a sequel to those examples of effective intra-Alliance cooperation.

The parent body of Panel 3, the Air Pollution Control Strategies and Impact Modelling Pilot Study, held its first meeting in April 1980, in Lindau, Germany. At that time the pilot study members developed an overall work program and organized several groups to implement it over a five-year period. The Working Group of the pilot study, chaired and co-chaired by the Federal Republic of Germany and the United States, respectively, has general responsibility for implementation of the work program and acts as a steering group for three panels: Panel 1, Emission Projecting (chaired by Germany); Panel 2, Air Quality Prediction (chaired by the Netherlands); and Panel 3, Environmental Impact (chaired by the United States). In addition, an ad hoc group, led by the Netherlands, will be responsible for the preparation of an overall scientific document on the source-to-impact cycle of selected groups of air pollutants.

The general objectives and work plan for Panel 3 were established by the ten NATO member countries at the first meeting of the Pilot Study in Lindau. The group agreed to produce a set of twelve documents on various aspects of emission measurement and inventory development, air quality prediction, non-

health effects on the environment, and source-to-impact cycles of selected air pollutants. Under the purview of Panel 3, four projected areas for documentation were identified.

These areas were air pollution effects on (1) materials, (2) terrestrial ecosystems, (3) aquatic ecosystems, and (4) climate and visibility. The task of the Panel was to address "sinks and uptakes of air pollution by the environment" and "consider the need for additional emission limitations of many pollutants." Panel 3 members were called upon to pool their resources to provide a more up-to-date documentation of non-health-related air pollution effects in the above four general categories.

The United States accepted the role of Panel Chair and invited other members to take the Co-Chair role(s). All NATO members were invited to participate in the Panel's work. At the April 1980 Pilot Study meeting, the following countries agreed to nominate members to Panel 3: Belgium, Canada, Germany, Denmark, Italy, the Netherlands, and the United States. Panel 3 has completed documents on air pollution effects on materials and terrestrial ecosystems. This report is the U.S. contribution to the third panel report, air pollution impact on aquatic ecosystems. Work on the fourth and final panel report, impact on visibility and climate, is under way. All NATO/CCMS documents are available through:

Information Service
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II. SEMINAR OVERVIEW AND CONCLUSIONS

A. Introduction

Atmospheric inputs to aquatic ecosystems cause changes that may be detrimental to man and his environment. A full understanding of this problem requires a global research program with clearly defined goals. At the conclusion of the Chapel Hill symposium on the atmospheric effects on aquatic ecosystems, the participants agreed on the need to

1) organize research so as to study total environmental quality rather than to independently investigate air or water quality;
2) recognize the true scope of the aquatic pollution problem as ranging from minor perturbations to massive devastation of aquatic ecosystems;
3) investigate the linkage between terrestrial and aquatic ecosystems;
4) establish continuous, long-range research programs that can ultimately predict environmental effects on a regional and global scale.

B. Overview of Aquatic Ecosystem Research Programs

In the United States, an interagency program to inventory and classify aquatic ecosystems has been under way for some time. A major consideration in this survey is the sensitivity of each ecosystem to acid deposition. Sensitivity can be estimated by measuring total alkalinity, a parameter that reflects the degree of incoming acidification and the ability of natural geochemical processes to buffer this acidity. The questions that are emerging from this study are: How many aquatic ecosystems have been or are likely to be seriously perturbed by present levels of atmospheric inputs? How quickly can an aquatic ecosystem recover from perturbation?

With respect to atmospheric effects, interactions between terrestrial and aquatic ecosystems within a watershed have not been thoroughly investigated. In some cases, acidic and metal-bearing particles deposited on vegetation and soil may be intercepted at the forest floor, without further transfer to surface runoff waters, and would consequently have little effect on associated aquatic ecosystems. The environmental conditions that support this buffering capacity are a combination of geological and hydrological features associated with the type of vegetation cover and organic content of the forest floor.

These concepts are directed at the important question: What types of atmospheric pollutants can be transferred from terrestrial to aquatic ecosystems?

Effects on plant and animal populations may range from changes in species diversity to the elimination of ecologically important populations and reversion to less complex successional stages. Species diversity may shift when a less tolerant population is replaced by a more tolerant one; however, perturbation will occur when a major food chain component, such as an aquatic macrophyte, is permanently eliminated. The remaining questions are: Which types of aquatic populations are most sensitive to atmospheric pollution? How will the loss of a single population affect the entire ecosystem?

These examples illustrate the need for expanding the scope of investigations beyond the traditional distinctions between aquatic and terrestrial ecosystems and between atmospheric and hydrologic pollution. One approach might be to investigate the entire hydrologic cycle, with a goal of monitoring the flow of pollutants through the entire global cycle, rather than merely the atmospheric or hydrospheric component of the biosphere.

Many studies of aquatic ecosystems are not carried out over a long enough time to ascertain fully the effects of atmospheric inputs. Atmospheric cycles are generally more rapid than those which take place in aquatic ecosystems. Also, meteorological events and aquatic cycles are superimposed on the process of succession in aquatic systems, a process which can require periods of several hundred years. Therefore, studies of two or three years' duration are not adequate to evaluate fully the impact of long-term atmospheric inputs.

For regulatory purposes, it is desirable to identify a few key parameters that can serve as indicators of the effects of atmospheric pollution on aquatic ecosystems. These parameters should have two characteristics: They should be linearly related to the effect on the ecosystem, and they should be controllable. An example might be sulfate concentrations in air as related to acid deposition. There appears to be a linear correlation between the amount of sulfate in the air and the acidity of deposition, and it is likely that sulfate emissions can be controlled.

C. Atmospheric Emissions and Deposition

Our ability to predict atmospheric inputs to aquatic ecosystems has been encumbered by our lack of knowledge of the mechanisms of deposition. Inputs, either gaseous or particulate, may be by wet or dry deposition. Dry deposition

is more predictable, because the deposition rate varies with air concentration and cyclic meteorological conditions, both of which can be determined with reasonable scientific accuracy. Models of dry deposition of gases have been developed using micrometeorological techniques, but are not yet reliable on a broad, regional scale due to uncertainties of deposition mechanisms. It appears that dry deposition of both gases and particulates may represent 40 to 80 percent of the total inputs to an ecosystem.

Wet deposition, on the other hand, is more episodic. Atmospheric pollutants that combine with water droplets during transport are removed by a process called rainout. Particles and gases are also removed during deposition by a process called washout. Consequently, the concentration of a particular pollutant in rain is partially related to the movement of the air mass through a source region and partially to atmospheric conditions at the site of deposition.

It is sometimes possible to relate observed deposition to specific sources on the basis of the chemical composition of deposited material. Models using source "fingerprints" have been developed that estimate the percent input from several industrial and natural sources. Typical residence times for particulate matter are 10 to 40 days in the case of both organic and inorganic pollutants.

Whereas it is difficult to model atmospheric deposition, it is not difficult to determine the recent history of deposition of organic components and metals. A chronological record of atmospheric inputs to aquatic ecosystems may be found in many freshwater and marine sediments, provided sufficient attention is given to collecting an undisturbed sediment core and to distinguishing between direct atmospheric inputs and surface runoff from the surrounding watershed.

D. Cycling Processes

Cycling processes within aquatic ecosystems have been investigated using natural radioisotopes (^{210}Pb and ^{210}Po) as tracers. These studies show not only the rates and sources of inputs (direct or surface runoff) but also the fate of elements in the water column. For metal particulates, removal from the aqueous phase is usually by sedimentation rather than with the outflowing water.

Studies of the cycling of energy-related pollutants in aquatic food chains have been conducted by the U.S. Department of Energy. It is anticipated that the results will be available in the near future.

E. Effects

For a pollutant to have an adverse effect on an ecosystem, it must perturb some natural process (energy flow, nutrient cycling) of the ecosystem to the extent that the ecological success of one or more populations is diminished. Any agent that causes a reduction in growth or reproduction of a plant or animal population could be termed a pollutant. Changes in environmental conditions, especially those affecting the nutrient medium, have no effect on an ecosystem until the ecological success of a population is reduced. When this occurs, a sequence of changes takes place that ultimately causes a perturbation of the entire ecosystem. Consequently, the first visible evidence of an effect of a pollutant on an ecosystem is usually seen as a reduction in growth of a population.

This "first effect" phenomenon can be anticipated by analogy to laboratory experimental conditions that predict a reduction in growth will occur at some level of pollution. The phenomenon can also be observed directly whenever growth or reproduction rates can be shown to be diminished, or the phenomenon can be discovered in retrospect whenever a population has disappeared and the species composition of the community shifts.

It is unfortunate that in reality, the earliest detectable effect of atmospheric pollutants on ecosystems is often a change in species composition. The acidification of ponds and small lakes, for example, frequently results in the disappearance of one or more populations of primary producers, making competition for space and sunlight less critical for plants more tolerant of higher acidity and sunlight. Animals are affected by direct physiological response to the acid environment, by increased susceptibility to disease and predation, by loss of prey and by loss of food when the primary producers are eliminated.

Ecosystems may be unbalanced or perturbed by broken links in the food chain, loss of other interspecific relationships, or abnormal disturbances in nutrient or nonnutrient cycles. For example, the mining of peat bogs may cause the sudden mobilization of trace metals resulting in possible toxic concentrations in aquatic ecosystems downstream from the bog.

Some effects of acid precipitation have been observed retrospectively in the decline and disappearance of populations in acidified fresh water systems of the Netherlands. Specifically, in ponds where Littorella uniflora, an aquatic macrophyte, grows abundantly at pH 6.5, Juncus bulbosus and Sphagnum cf cuspidatum replace Littorella at 3.8 to 3.9. When the waters reach 3.0,

all macrophytes disappear. It is believed that competition for mobilized CO_2 from the sediments may be responsible for this effect.

Fish and amphibians are also affected by lowered pH. Frogs, toads, and newts that normally have a wide distribution in Netherlands aquatic systems of low alkalinity have disappeared from ponds with a pH below 5.0. At this pH, frog eggs become susceptible to a fungus infestation. Fish eggs are also especially sensitive to perturbation by acidification.

Laboratory studies have led to a few generalized statements that can predict effects on fish populations. For example, low pH and high aluminum can cause stress in fish populations if the calcium content of the water is low. In general, fish reproductive processes and early life stages are the most sensitive to environmental perturbation. It is also an important point that organisms at several trophic levels may be affected simultaneously by acidified waters, and that the chain reaction normally caused by one population's response to a perturbation is compounded by additional effects at each succeeding level.

III. PRESENTATION SUMMARIES

During the two-day seminar, eleven presentations were made. They were arranged around the following four subtopics and presented in the order shown: aquatic ecosystem research programs, the mechanisms of atmospheric emissions and deposition, the cycling processes within aquatic ecosystems, and the effects of atmospheric pollutants on aquatic ecosystems. A summary of the presentations follows.

A. Aquatic Ecosystem Research Programs

In a presentation entitled "Aquatic Ecosystem Inventory and Research Program Assessment," David F. Brakke, of the Institute for Watershed Studies at Western Washington University, discussed the work of the National Acid Precipitation Assessment Program's Aquatic Effects Task Group. This task group works to meet five research objectives that will provide information needed to assess both short- and long-term effects of air pollutants on lakes, streams, groundwaters, and wetlands of the United States. It also seeks to describe how these effects can be alleviated at the site of the problem and what the ecological consequences of these remedial methods would be. Aquatic research will provide information regarding these questions:

1) What is the extent of sensitive and acidified lakes, streams, groundwaters, and wetlands in the United States?
2) What factors control the susceptibility of surface and groundwaters to acidic deposition, and how can these factors be used to predict future aquatic acidification or recovery under different loading rates?
3) What are the relationships between surface water acidification and biological processes, populations, and aquatic communities, and how can these relationships be used to predict ecological effects?
4) Does acidification of surface waters, groundwaters, or wetlands affect human health?
5) What mitigating (liming) techniques are best for short- or long-term restoration or protection of acidified lakes, streams, and groundwaters of the United States?

The recent accomplishments of the Aquatic Effects Task Group include:

1) An integrated assessment of the effects and extent of the acidification of surface waters due to acidic deposition;
2) Identification of the needs of aquatic biological effects research;
3) Implementation of a long-term program to monitor the chemistry and biota of surface waters in key sensitive areas of the nation; and
4) An evaluation of mitigation strategies (as well as the biological and chemical consequences of liming) for restoring or protecting lakes, streams, and their associated watersheds.

The program is making substantial progress in assessing the extent of the problem; initiating a comprehensive long-term surface water monitoring program; determining through stepwise assessments the geochemical linkages between terrestrial and aquatic systems; conducting biological effects studies that will result in regional prediction of future deposition levels; completing drinking water surveys of the eastern United States; and doing field tests to evaluate liming options.

A complex set of factors, such as bedrock geology, soils, and hydrodynamics of the watershed, governs the response of a body of water to acidic inputs. The response of biological populations is dependent upon changes in concentrations of several ions as modified by watershed processing. Research and modeling activities that will lead to linked chemical and biological models related to deposition levels are under way (see Figure 1).

Gary E. Glass, with the U.S. Environmental Protection Agency's Environmental Research Laboratory in Duluth, Minnesota, discussed the necessity of considering the hydrological cycle when establishing air quality criteria.

All living organisms are a part of the biosphere, as are all environmental interactions that affect these organisms. Some of these interactions involve biogeochemical cycles that pass nutrient and nonnutrient substances from one segment of the biosphere to another. The water cycle is probably the most important of these cycles because it is the medium through which many of the substances pass.

Environmental legislation in the 1960s and 1970s focused on the problems of clean air and clean water but did not clearly recognize the interaction between the two. The natural biogeochemical cycles that cleanse air and water

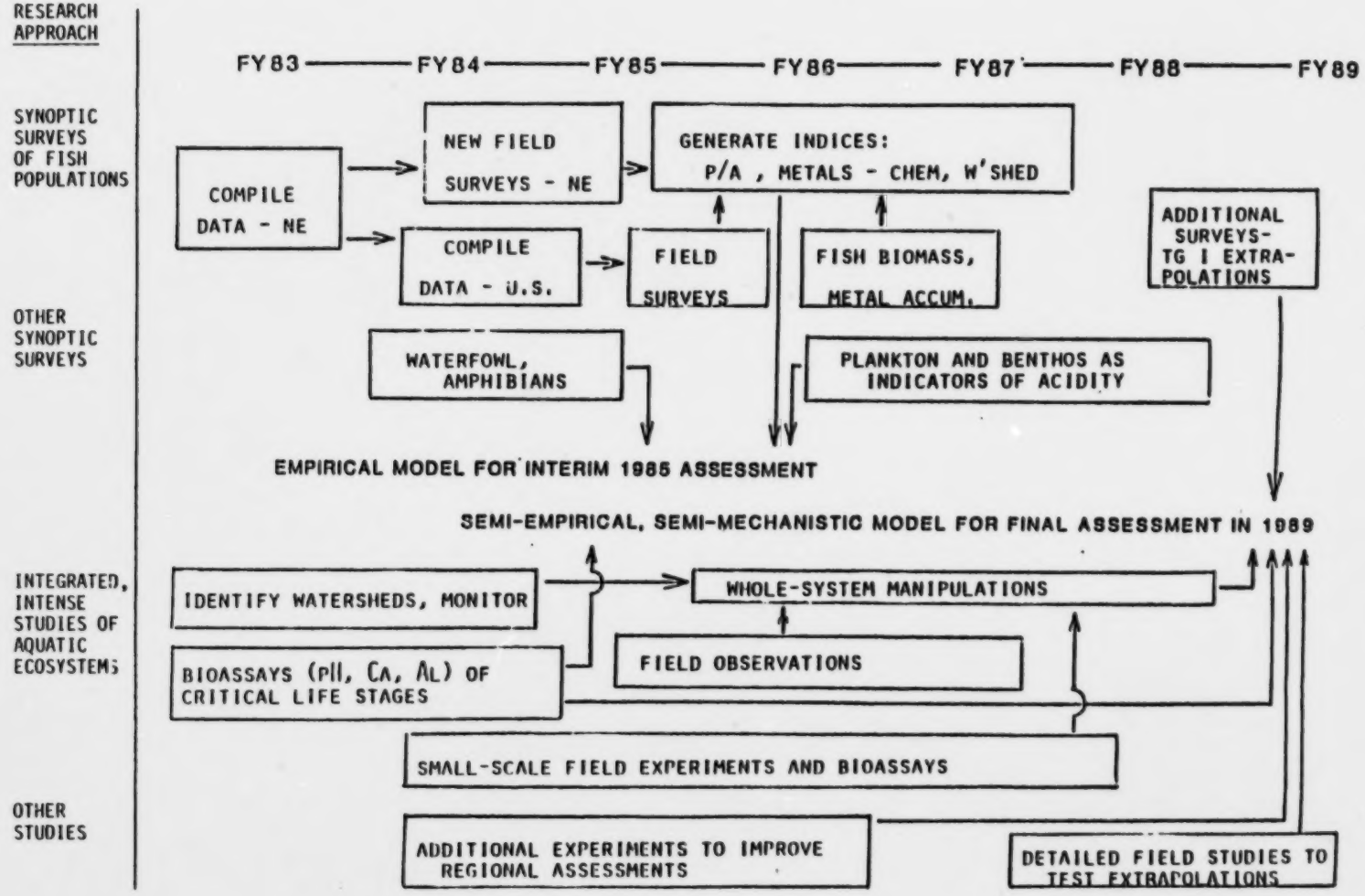


FIGURE 1. Aquatic effects task group plan of work

of pollutants are closely intertwined by the intricate mechanisms of the water cycle. In retrospect, it would have been more correct to control the pollution of the entire hydrocycle than to attempt to keep air and water clean independently.

There has been an increasing trend toward total global analysis of pollutants, a concept that fits well into the hydrological scheme. Water purifies the earth's atmosphere, recharges surface and ground waters, and provides a convenient dilution and assimilation capacity for manmade pollutants. The intentional use of the hydrological cycle by man to transport and transform pollutants is a process that can be closely monitored either by direct chemical measurement or by observations of organisms closely linked to the terrestrial and aquatic segments of the water cycle. Such monitoring occasionally gives an early warning of perturbation somewhat removed from the source of pollution.

Gaseous and particulate emissions are removed downwind either by direct adsorption on precipitation or by deposition on surfaces. Many of the pollutants deposited dry on surfaces return to the hydrocycle during the next rainfall as they are washed from the surface.

The point at which these dissolved pollutants begin to adversely affect the environment at the site of deposition may define the point at which regulation of emissions should commence. In a terrestrial ecosystem this point could most effectively be identified by monitoring the soil moisture solution available to plants or the ground water passing through the ecosystem. In an aquatic system, the water could be measured directly.

To some degree, there are buffers built into the hydrological cycle that prevent the continuous build-up of pollutants in the nutrient medium of organisms. For example, metals are bound by organic components of soil, making them less available to plant roots through soil moisture or aquatic ecosystems through surface runoff. Many pollutants are also removed by sedimentation in fresh and marine waters. The strength of these buffers determines the capacity of the global system to support the living components of the biosphere.

In no case does the interaction of air and water in the hydrocycle become more acute than with acidic deposition. Emissions of sulfur and nitrous oxides to the atmosphere are removed by rain or dry deposition at some point downwind, usually with a residence time of 10 to 15 days. The impact of this deposition depends not only on the intensity of deposition but on the nature

of the landscape. To understand the full process, it is necessary to interpret the full morphological, geochemical, and vegetational features of a watershed, all of which buffer the intensity of acidic deposition.

B. Atmospheric Emissions and Deposition

Bruce B. Hicks, of the National Oceanographic and Atmospheric Administration (NOAA), in a presentation entitled "Mechanisms of Air Pollutant Deposition to Aquatic Ecosystems," noted that deposition directly to exposed water surfaces contributes only a minor part of the total pollutant input to aquatic ecosystems. A much larger flux normally results from pollutants deposited on the surrounding countryside.

In many cases, a precipitation system will draw air from the more polluted mixed layer of the lower atmosphere and expose this air to substantially more effective in-cloud scavenging mechanisms. Thus, the deposition of pollutants in the precipitation is totally dependent on the amount of airborne material available to be scavenged and the efficiency of the precipitation scavenging process.

For trace gases, surface uptake is frequently controlled by the ability of the surface to absorb the specific chemical species. For snow and ice, the chemical composition of the surface has been shown to be important, and the presence of surface films or breaking waves is known to modify deposition to liquid water surfaces.

For submicron particles, the list of potentially contributing factors is much longer than for either trace gases or large particles. Consequently, the greatest uncertainties about dry deposition concern the case of aerosols. There is a paucity of field data, so laboratory studies form the foundation for many of the theoretical models that have been developed.

A water body surrounded by forest presents an intriguing contrast to the case of one surrounded by bare soil or sand. The vegetation of the forest will accumulate dry-deposited pollutants, and subsequent throughfall will be enriched accordingly. Dry deposition rates to bare soil will differ greatly from fluxes to the forest, especially for particles. Moreover, deposited pollutants are more rapidly available for chemical binding in the soil if the surface is not forested.

Detailed evaluations of pollutant fluxes into and out of "calibrated watersheds" have been advocated as a means of assessing dry deposition inputs,

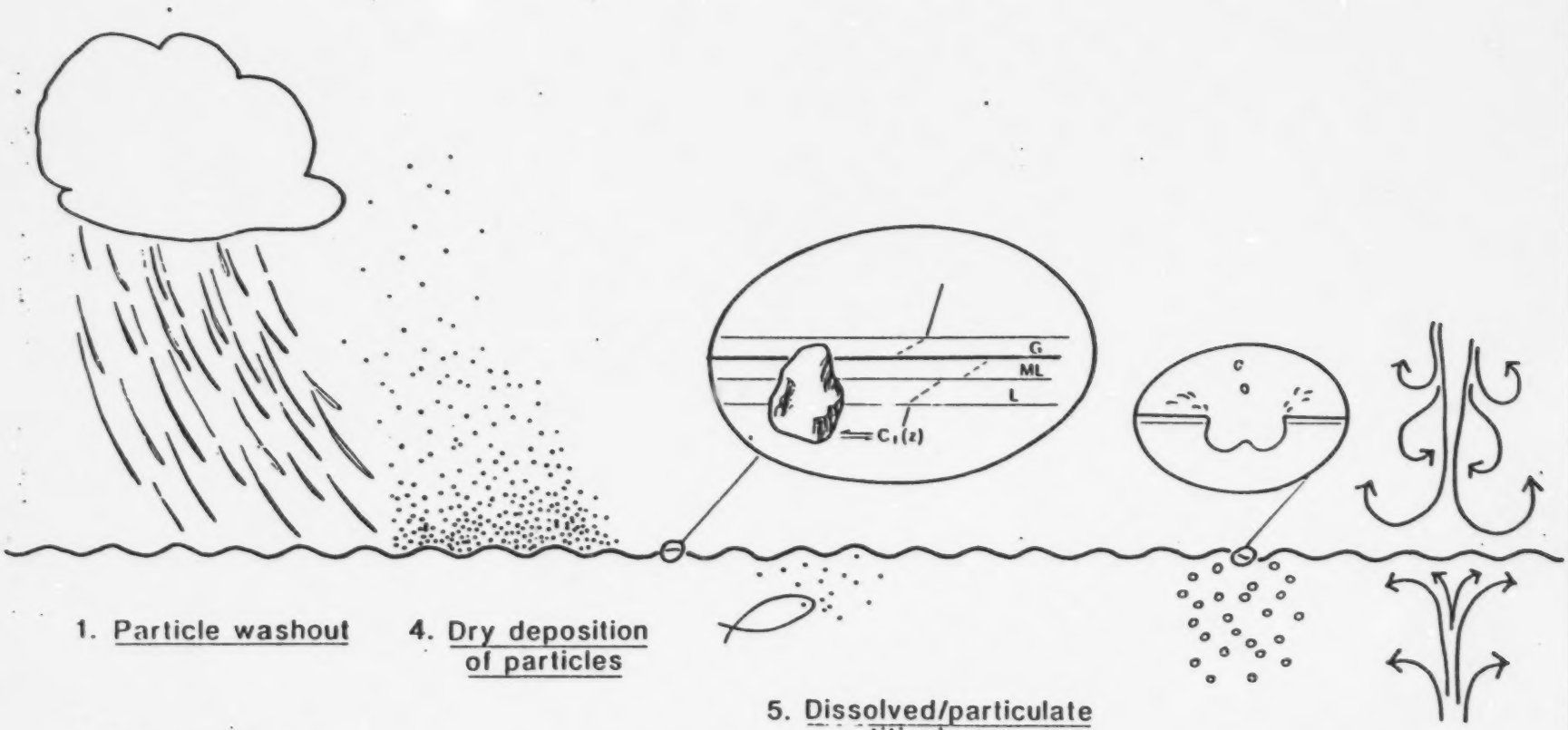
as the difference between output and measured wet deposition terms. In practice, several difficulties arise, especially concerning storage terms and corresponding time delays between inputs and outputs of the system, and the experimental precision which is required in order to permit differences between relatively large numbers to be interpreted with confidence. As a result of these concerns, the landscape-budget method has been infrequently applied, but is nevertheless the subject of ongoing intensive research.

In some special situations, and for some species for which very fast sensors are available, aircraft making use of eddy correlation methods can be used to measure fluxes to the surface. At this time, these aircraft methods are still in their infancy (largely because of a lack of suitable chemical sensors); recently, however, the possibility of being able to derive spatial averages directly and quickly has been sufficiently attractive to generate considerable developmental activity.

Steven J. Eisenreich of the University of Minnesota, in a paper entitled "Atmospheric Deposition of Organics to Aquatic Ecosystems," devoted the initial parts of the paper to a brief description of the atmospheric deposition processes. The latter parts were devoted to examples of how lake systems respond to atmospheric deposition and to recent results demonstrating how peat cores from bogs receiving their total input from the atmosphere (ombrotrophic) may be used to study organic deposition from the atmosphere to areas removed from sources.

Atmospheric deposition of trace organics to aquatic ecosystems has only recently been determined to be an important process contributing to the organic burden of lakes. The most dramatic examples of the importance of the atmospheric linkage has been provided by the Laurentian Great Lakes. For example, Eisenreich and others have summarized much of what was known about the input of airborne organics to the Great Lakes, especially Lakes Superior and Michigan. Recently, in the book Physical Behavior of PCBs in the Great Lakes, edited by Mackay et al., a summary appeared of current knowledge of the physical and chemical processes which influence input of organics to aquatic systems. Figure 2 shows a schematic view of the processes involved in the air/water transfer of trace organic substances.

Organic substances can be removed from the atmosphere by wet and dry deposition processes. The relative importance of each depends on the partitioning of the organic substances between the particle and vapor phases, the



1. Particle washout
2. Vapor washout
3. Vapor/particle partitioning
4. Dry deposition of particles
5. Dissolved/particulate partitioning
6. Vapor transfer
7. Bubble stripping
8. Bubble bursting

FIGURE 2. Air/water transfer processes

particle size distribution, the amount of rainfall, and basic physical/chemical properties such as vapor pressure, aqueous solubility, Henry's Law constant, and the degree of hydrophobicity, etc. Based on our knowledge of the behavior of hydrophobic organic substances in the Great Lakes, it appears that atmospheric inputs are often dominated by washout of particle-bound organic substances, and that surface losses are dominated by volatilization. D. Mackay describes the relationship between the two as a dynamic non-steady state, in that the processes are not directly linked, but approximately offset each other. This information points out the important need to study the processes of particle scavenging by precipitation and the volatilization of organic vapors from lake surfaces.

Other processes that may influence the air/water transfer of organic substances are bubble bursting and bubble stripping. As yet, we understand little of how these processes influence the cycling of organic substances in lakes. Of course, the adsorption/absorption of organic substances onto/into lake particles will affect the transfer processes. For example, the species of organic substances in water which volatilizes is that which is dissolved and not associated with aquatic detritus.

Trace organic pollutants exist in the atmosphere in the vapor phase and are adsorbed to suspended particulate matter. The processes by which trace organics are scavenged by precipitation and the amount ultimately deposited on the water/land surface depend entirely on the distribution of organic substances between the vapor and particle phases. Theoretical considerations suggest that vapor-aerosol partitioning in the atmosphere depends on contaminant vapor pressure, size and surface area of suspended particles, and the organic content. The less volatile the compound, the more it tends to associate with the aerosol particles and the more important role played by particle scavenging.

At present, however, sampling techniques do not adequately distinguish between vapor phase and particle phase species. The commonly used collection system employs a low-volume sampler in which air passes a glass-fibre filter followed by a solid adsorbent, usually polyurethane foam (PUF), XAD-2 macroreticular resin or Tenax GC.

MacKay's study includes numerous formulae for estimating various interactions such as vapor-aerosol distributions for chlorinated hydrocarbons, washout ratios of organic vapors and surface fluxes, rates of transfer, etc.

When estimating concentrations of trace organics expected to occur in wet deposition, it is important to consider the relative importance of atmospheric

removal processes. In general, 90% or more of the hydrophobic pollutants such as PCBs, toxaphene, etc., and effectively all high volatility compounds (e.g., chlorobenzenes) occur in the vapor phase. However, wet deposition is often dominated by the scavenging of particle-bound organic substances. So even though the bulk of the atmospheric burden exists in the vapor phase, deposition is dominated by aerosol/particle scavenging. This is consistent with the observation that highest concentrations of organic substances in rain occur within the first few minutes of the rain event. Snow is much less efficient than rain in scavenging aerosols and gases, so snow concentrations/ fluxes are often less than those of analogous rain periods.

A paucity of data exists on the occurrence of trace organic contaminants in the atmosphere. Only recently has an appreciation developed of the relative impact of atmospheric deposition on water quality (e.g., acid rain). Air masses circulating the globe become polluted by accumulating chemical components emitted from point and non-point sources. Air masses moving in a generally easterly direction transport airborne pollutants from urban/industrial centers to regions where deposition occurs. There are few areas of the earth which do not experience detectable concentrations of some atmospheric pollutants. Concentrations are reported for chlorinated pesticides, PCBs, PAHs, and phthalate esters in precipitation typical of rural areas around the world. The concentrations listed in Table 1, therefore, are expected to be typical for the Great Lakes environment but not necessarily derived from the region.

Recently, the annual inputs to and losses from Lake Superior were estimated. Atmospheric loading represents the majority of the inputs, while sedimentation and volatilization represent most of the losses. The data show that the inputs and outputs are in approximate balance, a situation which was clearly not the case for the past decades. The picture which developed for Lake Superior is that of a lake receiving the majority of its PCB inputs from the atmosphere, with a water column residence time on the order of 2-3 years. It is remarkable that a lake with a hydraulic residence time ~170 years can respond so rapidly to changes in inputs.

The sediment record provides comforting support to the hypothesis that the majority of PCB input is from the atmosphere. Figure 3 shows the total PCB profiles of three sediment cores taken at sites in Lake Superior differing in sedimentation rate by about eight times. In all cases, PCB concentrations in the cores occur at depths dated as about 1945-1950, with peak decreased concentrations observed in ~1972. Recent sediment shows decreased concentrations.

TABLE 1. AIRBORNE TRACE ORGANIC CONCENTRATIONS IN THE GREAT LAKES ECOSYSTEM[a]

Compound	Air		Precipitation	
	Range	Mean[b]	Range	Mean[b]
	(ng/m^3)		(ng/L)	
Total PCB	0.4-3	1.0	10-100	30
Total DDT	0.01-0.05	0.03	1-10	5
α-BHC	0.25-0.4	0.3	1-35	15
γ-BHC	1-4	2	1-15	5
Dieldrin	0.01-0.1	0.05	0.5-30	2
HCB	0.1-0.3	0.2	1-4	2
p,p'-methoxychlor	--	1	1-20	8
α-Endosulfan	--	1	1-10	2
β-Endosulfan	--	1	1-12	3
Total PAH	10-30	20	50-300	100
Anthracene	0.1-1	0.6	1.3-2.3	2
Phenanthrene	0.1-1	0.6	2.0-2.3	2
Pyrene	0.1-4	1.1	1.3-4.5	2
Benzo[a]anthracene	0.1-1	0.5	2.6-3.1	3
Perylene	0.1-2	0.6	--	1
Benzo[a]pyrene	0.1-2	1	0.1-3.1	2
TOC	$2\text{-}15 \times 10^3$	9×10^3	$1\text{-}4 \times 10^5$	2×10^6
DBP	0.5-5	2	4-10	6
DEHP	0.5-5	2	4-10	6

[a]Source: Eisenreich et al. (1981).

[b]Concentrations used to calculate dry and wet deposition.

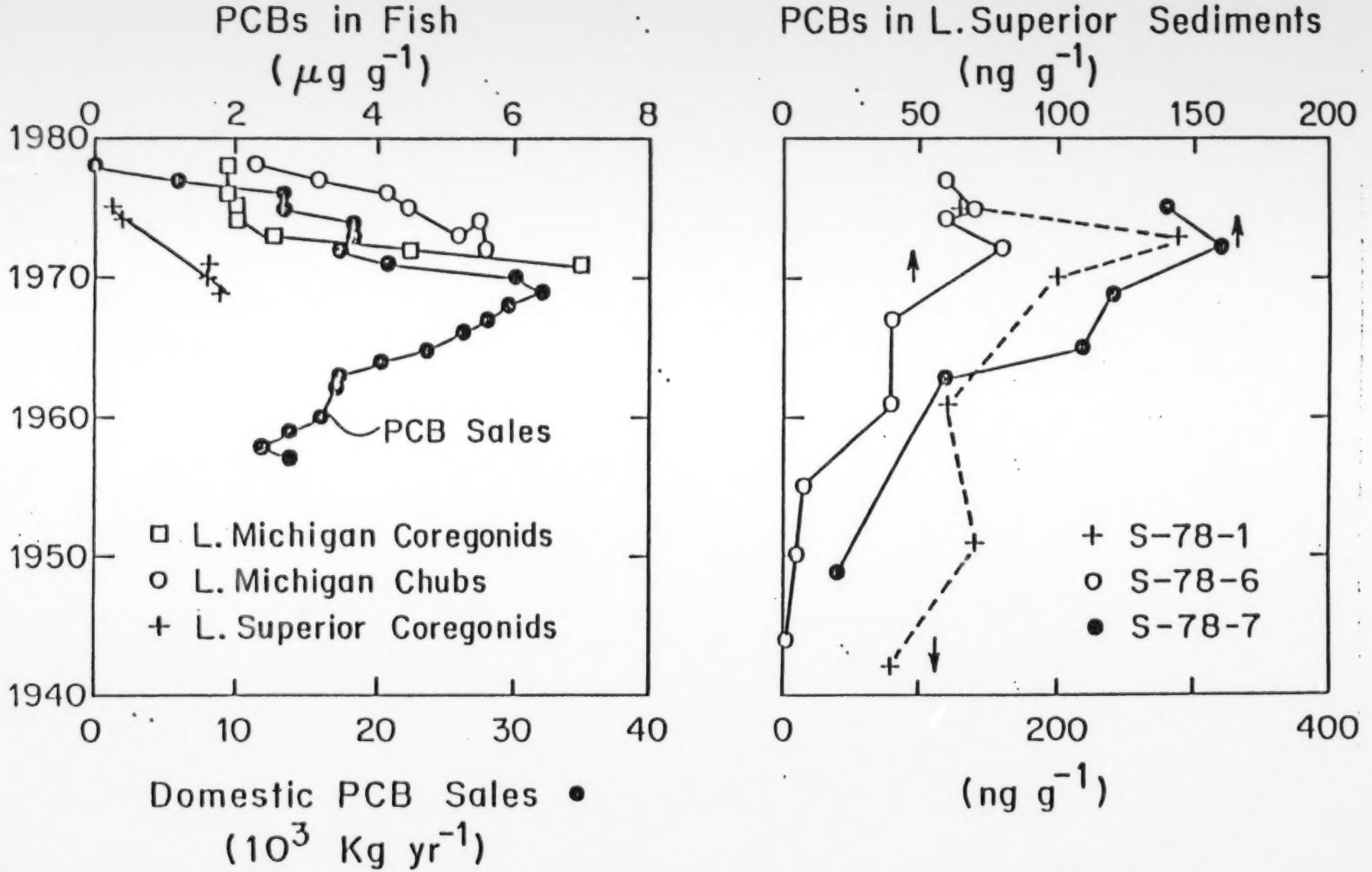


FIGURE 3. PCB profiles on three Lake Superior sites

This behavior is analogous to the decrease in PCB sales domestically, and the decrease in PCB concentrations in sediment postdates the decrease in PCB sales by ~2-3 years.

The story about DDT in Lake Superior may be somewhat different. DDT has been banned for use in North America since the early 1970s. Atmospheric and water concentrations appear to be increasing despite the ban. There is no evidence in the DDT profiles of three sediment cores taken in Lake Superior in 1978 that DDT is decreasing, whereas PCB inputs are clearly decreasing. A comparison of these sediment profiles with the domestic use of DDT in the United States suggests that inputs ought to be decreasing. It seems likely that domestic production of DDT has remained high, with the total amount being exported to developing countries. Though DDT is banned for use in this country, it is being exported and may be returning through atmospheric transport.

There is additional evidence that DDT inputs have increased in North America. Peat cores taken from west of Lake Superior, from bogs receiving their total input from the atmosphere (ombrotrophic), show increasing fluxes of total and "fresh" DDT. The fluxes appear to be within a factor of 5 of those estimated for a decade ago. PCB fluxes measured on the same cores are about the same as those observed for Lake Superior sediemnts.

In a paper entitled "Aerosol Exchange at Air-Water Interfaces: Comments on Source Reconciliation," Herman Sievering, Governors State University in Illinois, noted that models of air pollutant deposition at the air-water interface provide a sufficiently good description of reality to help direct research endeavors. However, these essentially steady-state models do not account for dynamic aspects of air-water aerosol exchange. For example, wind direction shifts cause periods of dynamic interaction between surface layer air and water waves which have been observed to be associated with the depletion of aerosol concentrations in this surface layer air. Models such as that of Slinn and Slinn (1980) predict air-water interface deposition of small aerosol (diameter, $D<1$ μm) to be at least tenfold less than that for large aerosol ($D>1$ μm). Yet, aerosol vertical gradient measurements over Great Lakes' surfaces suggest an only two to threefold difference in small versus large aerosol deposition. These predicted and observed discrepancies are quite significant since they imply an order of magnitude, or more, of uncertainty in pollutant aerosol deposition.

A major problem with modeling to date is its steady-state character, making it possible to model air-water aerosol transfer mathematically-but too

simplistically. Observation of meteorological and wave dynamics at the air-water interface should cause any careful observer to question steady-state modeling as being too simplistic and unrealistic, for dynamic exchange at the real air-water interface suggests that total aerosol deposition is greater than even recent modeling results would have us believe.

It must be concluded that careful field measurements of deposition velocity under a wide range of wind speeds and particle sizes, and at the actual air-water interface, is a future research necessity. Species-specific measurements are also a necessity since pollutant species such as Cd, Cu, Pb, and Zn may be observed to be depositing at the same time that the Ca, Mg, and Na lake-derived or sea-derived elements are emanating from large lakes or the sea. Indeed, eddy flux measurements at a marine location off the Florida coast by Sievering, Eastman, and Schmidt identified a predominant aerosol upflux even in the $0.2 < D < 0.5$ μm size range--the accumulation mode for anthropogenic particulate matter. Chemical characterization of aerosol confirmed that about one-third of the accumulation mode mass was sea salt, indicating that recorded upflux events are linked to surface sea salt production. However, the aerosol at the site is about half continental in origin--with both anthropogenic and soil components present. Figure 4 shows the very mixed chemical character observed in three different aerosol size ranges by SEM/X-ray analysis. An evaluation of aerosol transformation processes shows that particle growth and decay mediated by the relative humidity gradients present over the sea may have significantly altered the eddy flux results. Also, it hampers the quantitative interpretation of the data. Thus, it must be borne in mind that aerosol air-water transfer is truly a process of exchange and not only one of deposition.

In "The Role of Ombrotrophic Bogs in the Sorption, Storage and Release of Heavy Metal Airborne Pollutants," Curtis J. Richardson of Duke University reviewed the monitoring of ombrotrophic bogs (raised mires) as a method for analyzing regional air pollution problems. Of great concern is the increase in deposition of heavy metals from regional industrial centers and the long-range transport of heavy metals deposited by rain and dust. The development of an indexing system to determine the historical trends in heavy metal deposition on landscapes, as well as an analysis of the magnitude of anthropogenic versus natural inputs, is essential to the development of national and international management guidelines regarding air pollution standards.

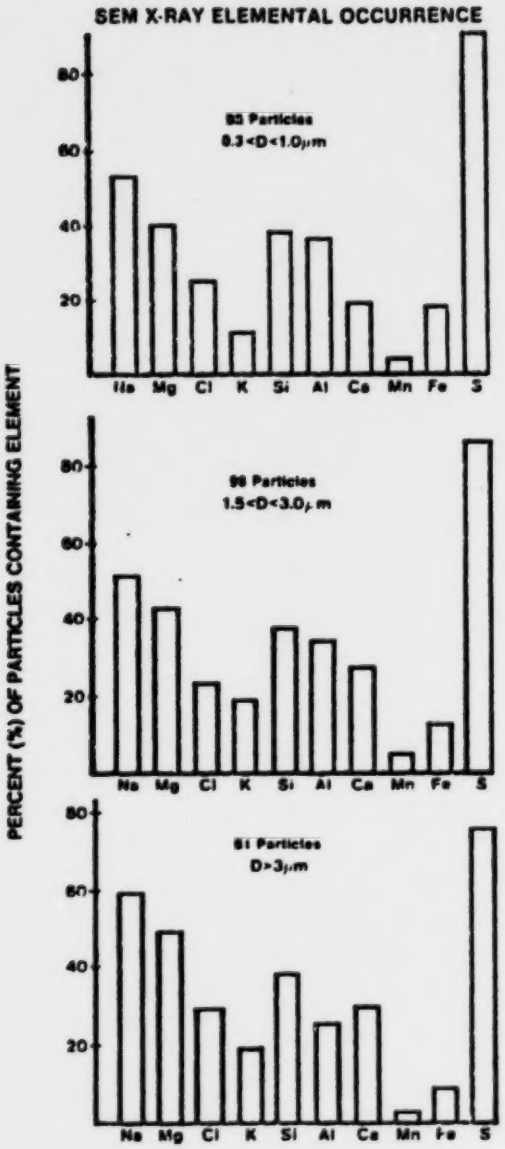


FIGURE 4. Occurrence of 10 elements in aerosol particles collected by a Casella impactor at Fowey Rocks and observed by a scanning electron microscope X-ray analysis. (From H. Sievering, et al., "Air-Sea Particle Exchange Measurements," Journal of Geophysical Research, 87:C13, 1127-1127 (1982).)

Ombrotrophic bogs receive elements only from atmospheric sources. It is well documented that living Sphagnum as well as peat have high sorption capacities, especially for heavy metals cations. Also, heavy metals from airborne pollution have been shown to be retained synchronously with peat formation in a series of studies in Europe, and that sorption capacity is more than sufficient to sequester efficiently atmospheric inputs. For many metals some translocation or redeposition takes place in the upper peat zone, due to plant uptake and changes in the water table (i.e., aerobic versus anaerobic conditions). However, the use of ^{210}Pb and ^{14}C has proven useful in establishing time-depth profiles which can provide a record of changes in heavy metal pollution to which the bog has been exposed. The chronological integrity of peat and the use of individual horizon dates allow one to calculate changes in deposition rate of heavy metals over time.

Atmospheric pollutants emitted from regional industrial centers and long-range transport of heavy metals deposited by rain and dust have been monitored in mosses (Sphagnum) in bogs throughout the world (see Table 2). The high cation exchange capacity of mosses relative to other plants provides an excellent retention mechanism for metals within the bog ecosystem.

The long-term retention and movement of metals in bogs is a function of the adsorption and desorption rates in the peat substrate, and of the permanent sequestering of ions in partially decomposed organic matter. The rates at which ions are adsorbed and desorbed and the competition between specific ions for exchange sites will determine their migration and accumulation patterns in the soil. Bunzl et al. (1976) in an excellent analysis of the kinetics of ion exchange in peat for Pb, Zn, Cu, and Cd, showed that the absolute rates of absorption increase as more metal ions are added. This study also showed that the half times of adsorption also decreased as an increase occurred in the metal added. From Bunzl's study and laboratory analysis of adsorption rates for other metals, it was determined that the retention of heavy metals by peat followed the following order of preference: Pb<Fe<Cr<Cu<Cd<Ni<Zn. In addition, Hg proved to be the most immobile of all the heavy metals tested.

To obtain an estimate of the rate of accumulation of heavy metals in peat bogs requires that a dating procedure be employed which is accurate, especially over the past two hundred years. Several authors have suggested that short-lived natural radioisotopes such as ^{210}Pb (half-life 22.6 yr) can be used to date and estimate accumulation rates for bog peats if the data are reinforced with standard analysis for the area.

TABLE 2. MEAN ELEMENT CONCENTRATIONS (MG/KG-DRY WEIGHT) SPHAGNUM SPP. FROM SCANDINAVIAN AND NORTH AMERICAN BOGS (modified from Furr et al., 1979)

ELEMENT	NEW YORK STATE ADIRONDACKS	WISCONSIN[1] MINNESOTA	GREAT SLAVE[2] LAKE, NWT, CANADA	NORTHERN FINLAND	SOUTHERN FINLAND	SOUTHERN[3] SWEDEN
Zn	81	33	104	34	47	88
Cu	27	6.8	3.0	6.3	3.8	5.0
Pb	78	23	0.9	5.6	29	80
Cr	227	--	0.6	5.0	2.6	3.3
Ni	1.6	--	0.2	1.2	1.7	3.6
Cd	0.3	--	0.2	0.3	0.5	1.2
Hg	0.11	--	0.04	0.04	0.06	--
Co	6.2	10	--	--	--	0.7
Mo	12	15	--	0.5	--	--
Mn	86	300	53	169	56	65
Fe	4182	620	83	231	401	1416

[1]Gorham, E.; Tilton, D.L. (1978) The mineral content of Sphagnum fuscum as affected by human settlement. Can. J. Bot. 56:2755-2759.

[2]Pakarinen, P.; Tolonen, K. (1977) Distribution of lead in Sphagnum fuscum profiles in Finland. Oikos 28:69-73.

[3]Ruhling, A.; Tyler, G. (1971) Regional differences in the deposition of heavy metals over Scandinavia. J. Appl. Ecol. 8:497-507.

Peat profiles for two bogs in Denmark yielded intriguing data. Based on the assumption that heavy metals such as Zn, Cr, Cd, Cu, and V would be fixed to the peat substrate, Jacobsen (1982) calculated the metal deposition rate for the Draved Mose Bog (Figure 5). A general increase in the rate of deposition for the previously mentioned metals was found, but the increase during the 20th century differed for each metal. Nickel increased dramatically during the last decade while Cd showed a steady increase throughout the 20th century. Zinc, Cr, Cu and V increased primarily after World War II, a trend which followed the increase in fossil fuel consumption. The data from this series of bog studies strongly support the contention that ombrotrophic peatlands sorb heavy metals and that the careful analysis of peat profiles provides an historical index of airborne pollutants.

In summary, it appears that metals are retained synchronously with peat deposition and that peat sorption capacity is more than sufficient to efficiently sequester atmospheric inputs of heavy metals. The use of ^{210}Pb looks promising as a dating system for establishing a realistic time-depth scale during the last two centuries in undisturbed ombrotrophic bogs.

In another case, a preliminary analysis of the vertical distribution of heavy metals in North Carolina pocosin* wetlands was undertaken by Daniel (1978) using U.S. Geological Survey data. Atomic adsorption spectroscopy, x-ray fluorescence spectroscopy, and neutron activation analysis were done on pocosin peats by the United States Geological Survey Analytical Laboratory. Typical patterns for heavy metals and Si are shown in Figure 6. The influence of the mineral substrate on the metal content of the peat is found around the 300-cm depth, where the highest Si levels are recorded. In general, the highest levels of Hg, Pb, Cs, Cd, and Zn are found in the top 50 cm of peat. In contrast, the highest levels of Ni and Cu are found at the base of the peat deposit, an area influenced by the underlying mineral strata. Seven elements were found in concentrations greater than their clarke values (or average crustal abundance) in a majority of the twelve cores.

A major objective in this research area is to identify the effect of pocosin drainage and subsequent oxidation of peat on the release of heavy metals into adjacent aquatic ecosystems. A recent preliminary survey of water

*pocosin: an Algonquin Indian word meaning "swamp-on-a-hill," denoting swampy or marshy, but especially in reference to upland ombrotrophic shrub bogs occurring on the southeastern coastal plain of the United States.

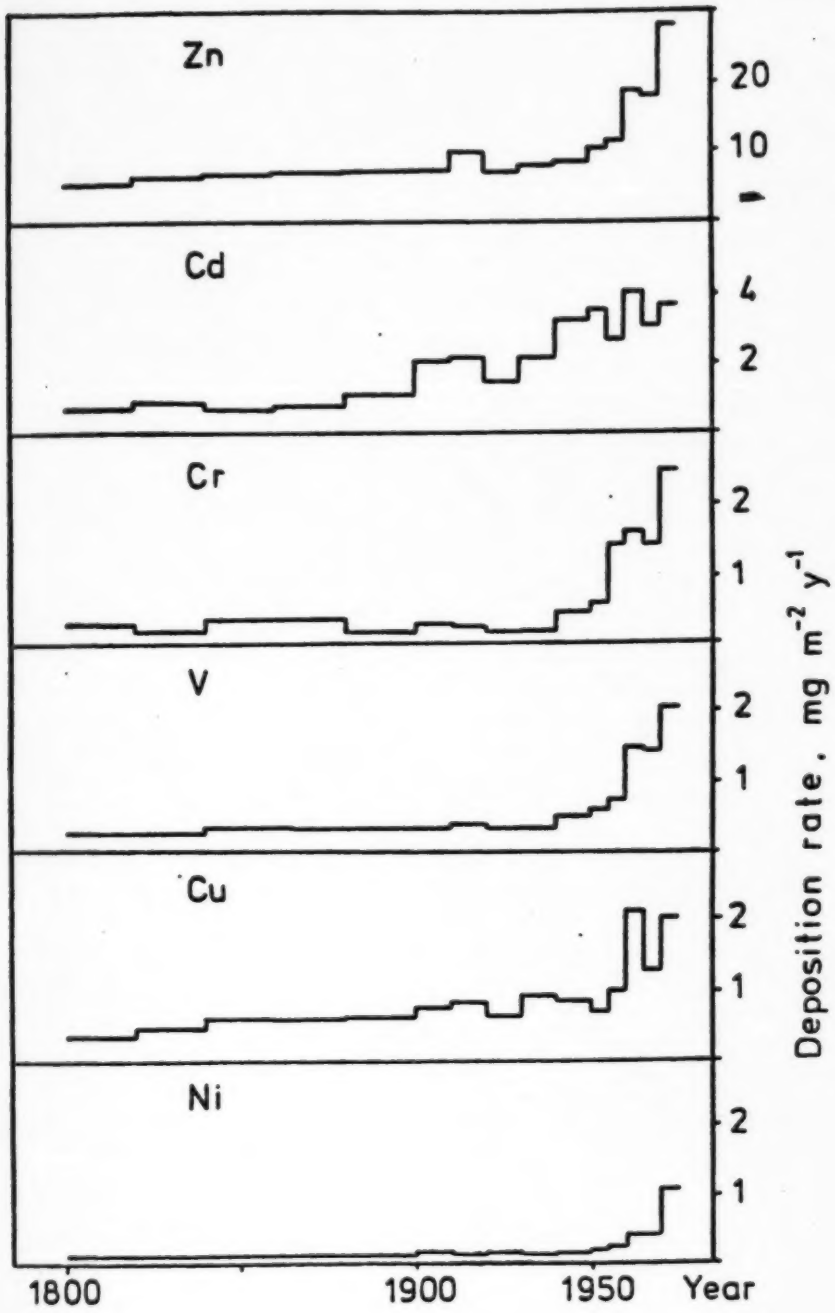


FIGURE 5. Calculated metal deposition in Draved Mose. (From Jacobsen, O.S., "The Historical Development of Air Pollution as Reflected in Ombrotrophic Peat Bogs in Denmark," in Ecosystem Dynamics in Freshwater Wetlands and Shallow Water Bodies: Proceedings, Scope-UNEP: 1982, pp. 271-289.)

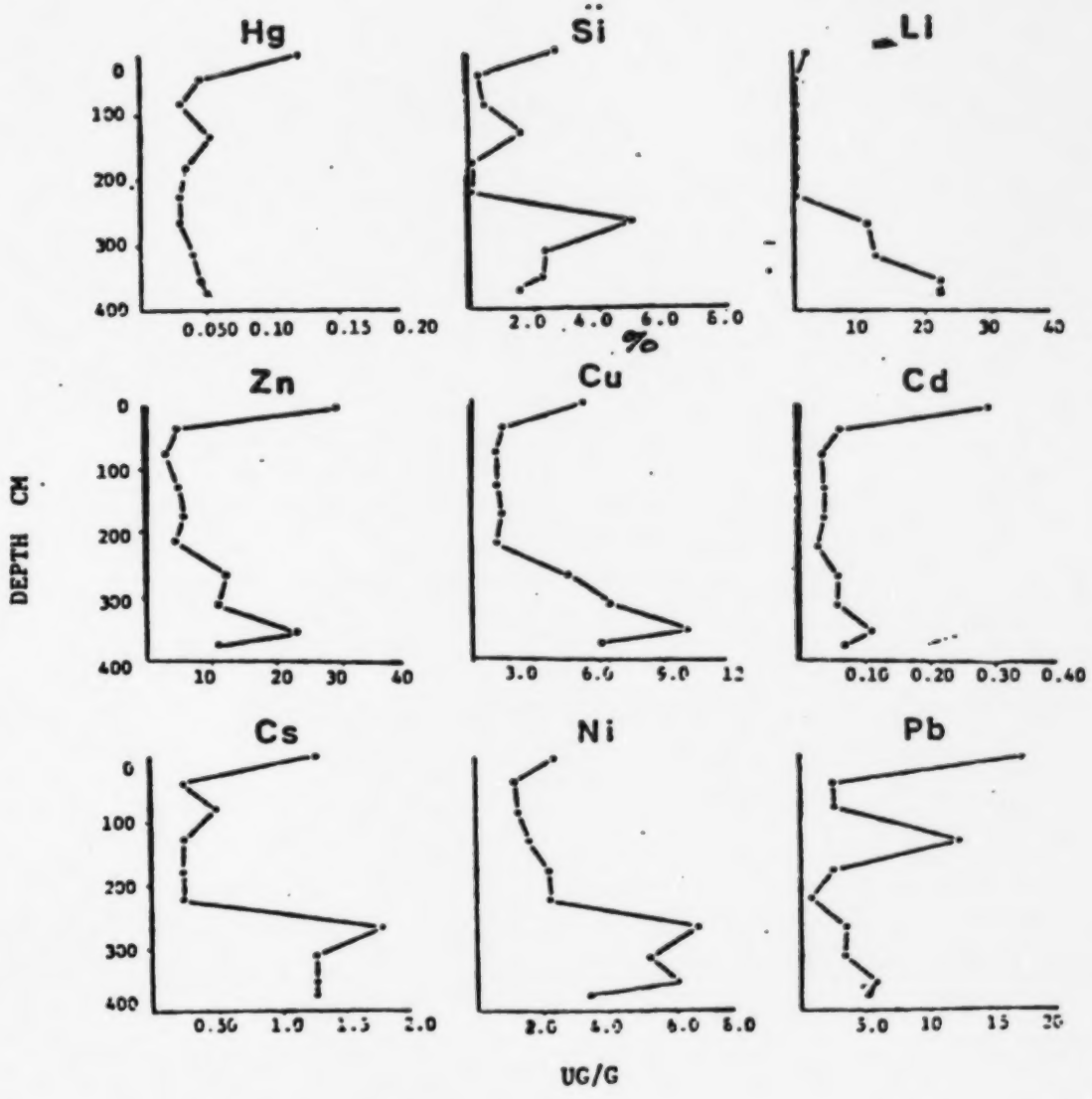


FIGURE 6. Profiles of heavy metal concentration in pocosin peatlands in North Carolina (Adapted from USGS data.) (From Daniel, P.B., "The Occurrence and Distribution of Elements in a Modern Coal-Forming Environment on the Atlantic Coastal Plain in Dare County, N.C.," Columbia, S.C.:Univ. of S.C. Master's Thesis, 1978.)

quality from output canals of an area being drained for peat mining in North Carolina revealed elevated levels of Hg, Pb, Zn and Cu (Table 2). The concentrations of Hg in the canals greatly exceeded both U.S. Environmental Protection Agency and state standards. A significant increase in total dissolved metal content for Pb, Cd, Zn, Co, and Mn was also reported for canal water which drained from developed peatlands versus water from undisturbed peatlands in southern Florida.

All of these studies indicate that drainage of peatlands which have sequestered heavy metals over the past few centuries may result in significant outputs of potentially toxic materials to receiving waters. The effects that these heavy metals will have on the aquatic ecosystems and their biota are unknown. What is known is that estuarine systems are particularly vulnerable to contamination by heavy metals, due to the bioaccumulation and biomagnification of metals such as Hg. For example, filter-feeding mollusks are particularly efficient at accumulating Hg from contaminated sediments. Methylation of Hg and biomagnification in the trophic system can present a hazard for many years after the elimination of the heavy metal input. It is clear from the abundant literature that heavy metal contamination of aquatic ecosystems is a severe ecological problem that can result not only in the loss of species and breeding grounds, but the contamination and subsequent loss of entire commercial fisheries.

Ombrotrophic bogs receive elements only from the atmosphere and have high sorption and storage capacities for heavy metals. If these ecosystems are undisturbed and the peat profiles are properly aged, they can provide historical evidence as to the changes in anthropogenic inputs of heavy metals during the past few hundred years. The storage of heavy metals in bogs and their subsequent release through drainage of these ecosystems can result in significant increases in metal input into adjacent or downstream aquatic ecosystems. The full ecological consequences of these releases are for the most part unknown.

C. Cycling Processes

A paper entitled "The Use of Natural Radioisotopes as Tracers for the Cycling of Airborne Pollutants in Lakes," prepared by M.M. Tilzer and H.H. Stabel of the Limnological Institute, University of Konstanz, and I. Appel and A. Mangini of the Institute of Environmental Physics, University of Heidelberg,

Federal Republic of Germany, and presented by M.M. Tilzer, reported upon studies of internal pools and fluxes of two closely interrelated natural radioisotopes (^{210}Pb and ^{210}Po) in Lake Constance (540 km^2; 100 m mean depth). These studies assessed rates of inflow from the main tributary, seasonal shifts of particulate and dissolved pools, and rates of losses via sedimentation and outflow, as a means of estimating the relative contribution of direct atmospheric precipitation to the total inputs into the lake. Mass-balanced models have been constructed which allow estimates of the relative significance of atmospheric precipitation as a source which otherwise can only be estimated with great difficulty. It is shown that about 50% of the ^{210}Pb pool in the lake originated from atmospheric sources whereas ^{210}Po influx via precipitation was insignificant. Natural radioisotopes, then, can serve as tracers for airborne pollutants whose behavior within the system can be assumed to be similar but whose cycles cannot be assessed with comparable accuracy.

In a paper entitled "Energy-Related Pollutants in Cayuga Lake, New York, and Adirondack Preserve, New York Aquatic Ecosystems," written by Merrill Heit, Catherine Klusek, Kevin Miller, Yulin Tan, Doris Sutton, Patricia Legotte, and William Rosa from the U.S. Department of Energy and by John Burke from the Woods Hole Oceanographic Institute, the authors report on some pertinent results from studies now under way at the Environmental Measurements Laboratory (EML). These studies are aimed at evaluating the inputs into aquatic ecosystems of combustion-related pollutants from both local and long-distance sources. Measurement of pollutants from a local source, a coal-fired power plant, is described for Cayuga Lake, New York. Also, the occurrence of long-distance transported pollutants is being investigated in remote acidic lakes in the Adirondack Preserve of New York.

Cayuga Lake, located in the New York Finger Lake region approximately 21 km northwest of Ithaca, is the site on the east bank of the Milliken coal-fired electricity-generating station. The plant began operation in 1955 and consists of two tangentially-fired 25-megawatt coal combustion units. Electrostatic precipitators were installed in 1976 and are said to have an efficiency of 99.7%.

The surface sediments of all acidic Adirondack lakes so far investigated show markedly higher concentrations of several trace elements and polycyclic aromatic hydrocarbons (PAH) in their surface sediments when compared to those taken at depth. Although there is some variation between lakes, in general,

elements that show this trend are As, Cd, Cu, Pb, Sb, Se, V and Zn and all of the parental (non-alkylated) PAH with the exception of perylene. These trends are shown in Figures 7 and 8, respectively. Figure 7 shows a decreasing trend with depth for Pb in five Adirondack lakes. It is significant that although all five lakes show this trend, the maximum Pb concentrations found in the lakes differ markedly. For example, Woods Lake was found to have a Pb concentration of 138 µg/g (dry weight) at the surface while Sagamore only had 59 µg/g dry weight. Similar results are shown in Figure 8 for all of the combustion-produced PAH. For example, fluoranthene was found to be present at 1236 ng/g in the surface of Woods Lake, but occurred at only 463 ng/g in Sagamore. These differences in concentration are due apparently to differences in the sedimentation rates in the lakes and are eliminated by comparing the pollutants by their integrated deposition per unit area, e.g., $\mu g/cm^2$. When applied to the two examples previously given, the differences between Pb and fluoranthene in Woods and Sagamore Lakes are eliminated, with almost identical amounts of these substances deposited in each system. Such comparison also suggests that the inputs of these substances from local sources are negligible when compared to region-wide deposition, since Sagamore and Woods Lakes are separated by about 30 km and yet have similar amounts of pollutants deposited in them.

In another study the intent was to identify the particulate-associated elemental and organic inputs from the Milliken coal-fired power plant into the Cayuga Lake aquatic ecosystem. The results showed, however, that except for a small area confined to the stacks, the coal plant made no discernible contribution to trace element or PAH levels in Cayuga Lake. It appears that the stack emissions are either masked by other sources or atmospherically transported and deposited elsewhere. The highest levels of PAH were found in marinas and areas of the lake receiving urban runoff. Inputs from these local sources were found to decline in concentration very rapidly with distance from their sources. The results from this study clearly suggest that region-wide atmospheric deposition is the prime source of polycyclic aromatic hydrocarbons entering the lake environs. Trace element and radionuclide mass balance studies at Milliken station supported this view.

Recent sediment coring studies have shown that the major inputs, i.e., flux, of PAH into the Cayuga Lake ecosystem occurred prior to the Milliken station start-up in 1955. This is clearly shown for the PAH fluoranthene in

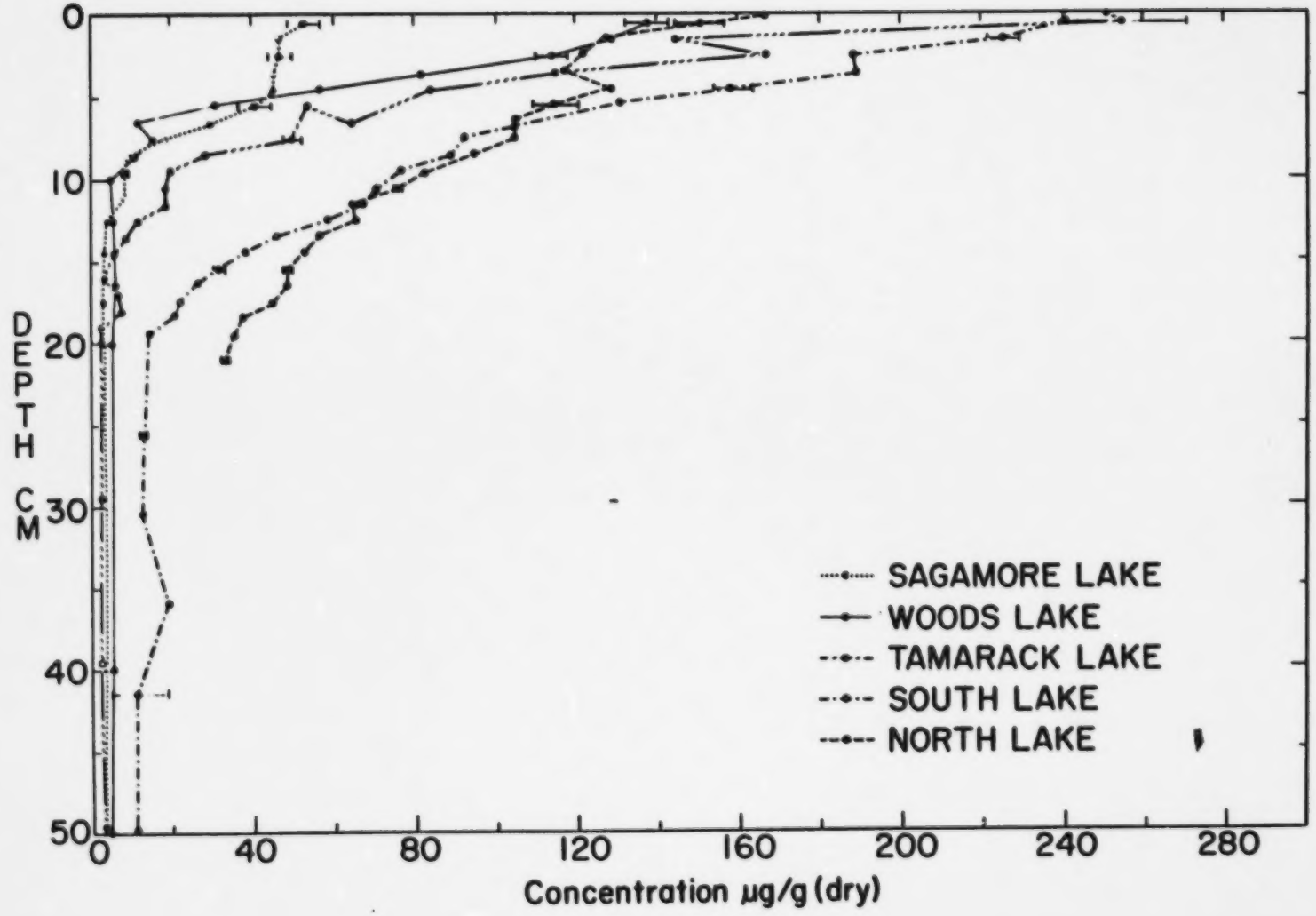
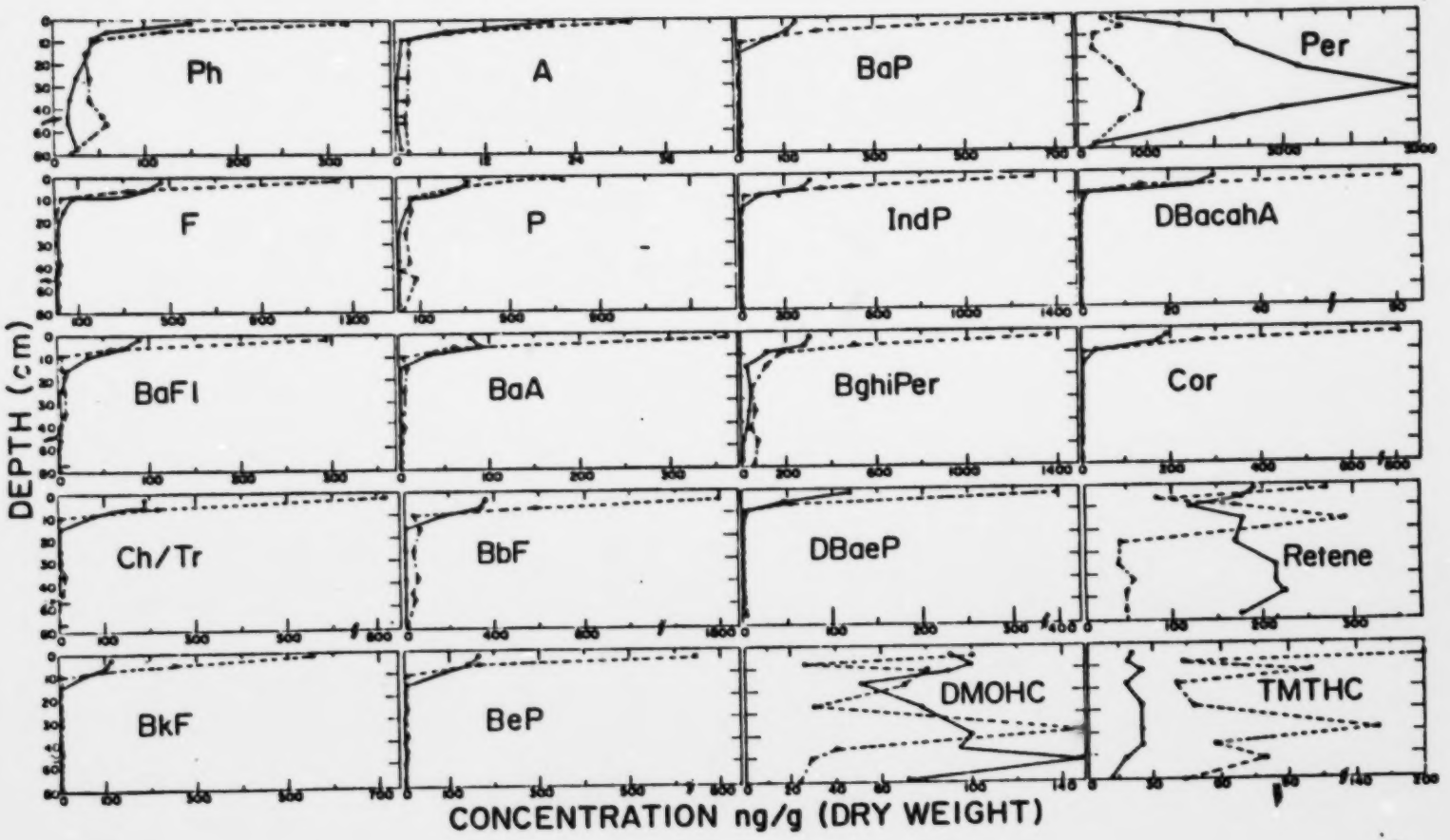


FIGURE 7. Lead distribution in Adirondack lake sediments



Key

● = Sagamore Lake

O = Woods Lake

FIGURE 8. PAH depth distribution in woods and Sagamore lakes

Figure 9, where the maximum flux occurs about 1953 with a sharp decline through to the present. The Pb flux into the lake has declined since the early 1970s.

Interestingly, in Cayuga the increased flux of both trace elements and PAH appears to have begun prior to 1900, agreeing well with the ^{210}Pb dates projected for the Adirondacks acid lakes. Since the Finger Lakes region has been shown to receive acidic precipitation and by inference particulate-associated combustion products such as metals and PAH, the data suggest that the input of these materials into the environment appears to have decreased in the last 10-30 years.

D. Effects

In a paper prepared by C. den Hartog, J.G.M. Roelofs, J.A.A.R. Schuurkes, and R.S.E.W. Leuven of the Laboratory of Aquatic Ecology, Catholic University, Nijmegen, The Netherlands, and presented by C. den Hartog, the effects of acid precipitation on freshwater systems in the Netherlands were discussed.

These effects are most spectacular in the poorly buffered soft waters with mineral sand bottoms that are practically devoid of lime. These waters are normally characterized by dominance of isoetids, particularly Littorella uniflora, but under influence of a decreasing pH, the inorganic carbon budget becomes disturbed, leading to suppression of Littorella by Juncus bulbosus and/or Sphagnum cf cuspidatum, and finally to the disappearance of all macrophytes.

Further, these waters become unsuitable for fish and amphibians. In the case of the amphibians the reproductive success is negatively affected by low pH. Most frogs, toads, and newts have a rather wide range of occurrence when correlated with alkalinity, and acidification of the soft waters means to them only a shrinkage of the available area. To Rana arvalis, which has its main distribution in low alkalinity waters, acidification brings about the danger of local extinction.

The acidified waters appear to be unsuitable for commercially important fish species. The commercially unimportant Umbra pygmaea is the most tolerant fish species.

Another effect of acid precipitation on hard water systems, particularly in dune pools, is "hardening" of the water due to dissolution of $CaCO_3$ from the bottom. The recent discovery in several dune lakes of Potamogeton coloratus,

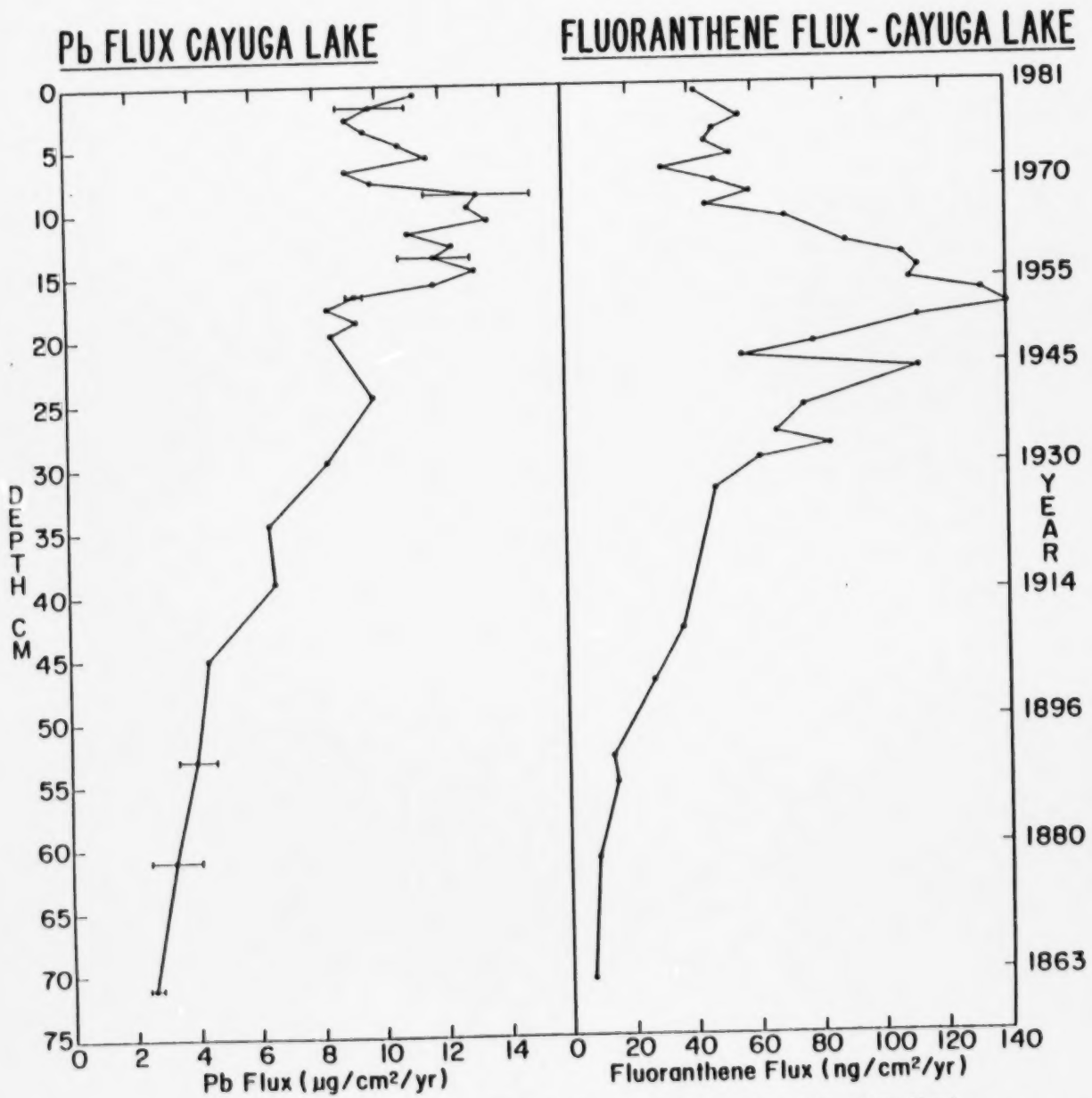


FIGURE 9. Lead and fluoranthene fluxes in Cayuga Lake, New York.

a very rare species in the Netherlands, may be a secondary effect of water hardening.

Floyd C. Elder of the Aquatic Physics and Systems Division of Environment Canada reported on the impact of acid precipitation on aquatic regimes of Canada. The pH of precipitation over Canada ranges from about 4.2 in the St. Lawrence basin to greater than 5.5 in the far north and prairie regions. This pH has been associated with SO_4 and NO_3 excesses of up to 40 m-moles/m^2. However, analyses of the excess values found in surface waters has been interpreted to indicate that SO_4 is primarily responsible for the alkalinity deficits in these waters.

Analyses of the empirical studies of biological and chemical alterations and application of ionic balance models have provided a preliminary estimate of the SO_4 deposition that appears to lead to aquatic regime damage in areas where buffering capacity is small. A "target loading" objective for SO_4 in wet deposition has been established as 20 kg/ha.yr. Description of the biological losses in terms of fisheries, wildlife, and lower order productivity are presently being developed in terms of systems models.

Geochemical, biosystem, and physical basin parameters have been incorporated into a multiparameter index of sensitivity to acidification. These parameters have been assessed and evaluated for Eastern Canada in terms of sensitivity maps, and preliminary assessment of the magnitude of the resources at risk for that portion of the country has been completed.

Finally, in "Lake Sediment Studies: An Historical Perspective of the Chronology and Impact of Atmospheric Deposition," Stephen A. Norton from the University of Maine showed that atmospheric pollution and deposition of the pollutants in dry- and wet-fall are well established as a general phenomenon in the northern hemisphere. Of particular interest are the chronology, the spatial distribution, and the concentration time-trends of the phenomena. Heavy metals (e.g., Pb, Zn, and Cu) constitute one group of pollutants whose emission and deposition rates far exceed natural rates for eastern North America and western Europe; the fluxes of several of these elements far exceed those of natural biochemical cycling (Galloway et al., 1982). However, systematic spatial and temporal measurements of these metals are not available for ecosystems in general. Many of the data which exist for the distribution of these metals have been gathered from grossly polluted sites where point sources exist. However, certain "pristine" environments, notably ombrotrophic bogs,

lake sediments, and forest soils, offer hope for reconstructing the history of atmospheric pollution on a regional scale.

This report described the type and characteristics of information that can be derived about metal deposition and mobilization from these three habitats (with an emphasis on lake sediment).

In the deep part of lakes, sediment accumulates more or less continuously. Cores of undisturbed sediment can be retrieved; they can be analyzed for their chemical and biological contents; and the different levels can be dated by use of the radionuclide ^{210}Pb.

The chemistry of a particular depth interval of sediment is determined by a number of factors, including

1) The chemistry of material eroded from the drainage basin and deposited at the coring site, as well as material deposited from the atmosphere;
2) Net sedimentation of material derived from within the lake, including organisms (diatom tests, invertebrate remains), resuspended sediment;
3) Additions, losses, or relocation of inorganic and organic matter from the sediment, after deposition. These changes are generally greatest at or near the sediment/water interface for oligotrophic lakes and decrease abruptly to near zero by ~5 cm in the sediment.

Lakes appropriate for the study of atmospheric deposition of pollutants generally have come under investigation only in the last 10 years, due largely to the interest in acidic precipitation and its effects. The lakes under study are generally in remote sites to avoid other disturbances and confusing factors.

Figure 10 gives a chemical profile of a sediment core from a typical undisturbed acid-sensitive lake in northwestern Maine. The ^{210}Pb profile (pico Curies/gram of dry weight versus depth) can be used to establish the age of the sediment (e.g., 6 cm $\tilde{}$ 1880). The following general conclusions can be reached by consideration of this figure:

1) Most of the major elements (e.g., Ti) display relatively constant concentration, suggesting constant conditions in the drainage basin.

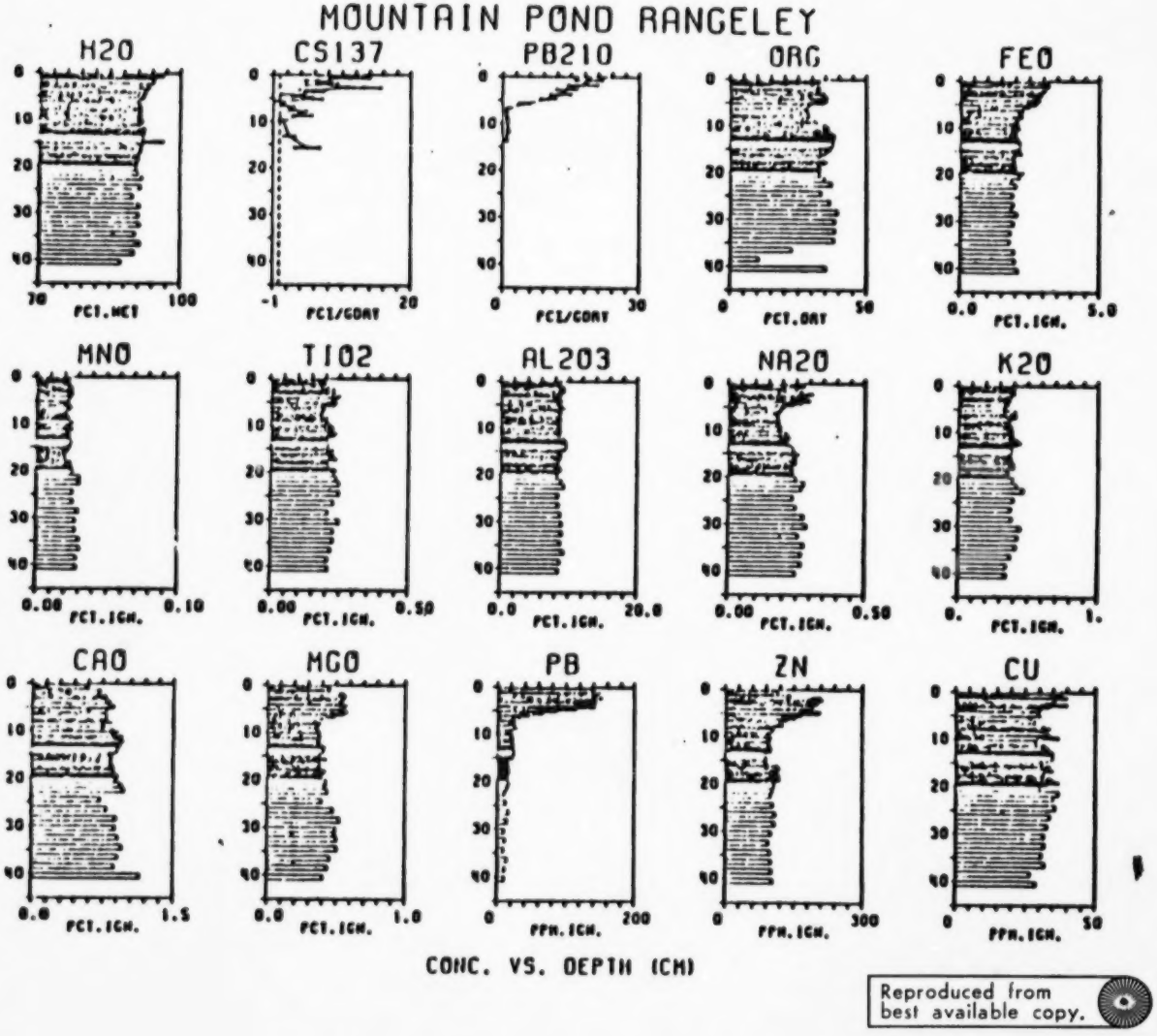


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FIGURE 10. Sediment core chemical profile

2) Pb starts increasing independently about 1850. The concentration levels out in more recent sediment, but the deposition rate continues to increase until about 1970. The Pb profile above 10 cm is dominated by atmospheric input.

3) Zn increases concurrently with Pb, but in recent sediment it decreases. This is attributed to acidification of the lake water (because of acidic precipitation) with associated leaching of the Zn from the sediment detritus, before or after deposition. This conclusion has been reached independently by scientists in Sweden, Finland, and the U.S. This general relationship holds true for all lakes which are receiving acidic precipitation and which have low pH ($\tilde{\sim}$ 5.5).

Lake sediment studies reveal essentially synchronous onset of regional atmospheric deposition of metal pollutants in eastern North America (1875 ± 25 yr) and in Scandinavia (slightly earlier). Pb sediment deposition values increase to about 1970, with a suggestion of either a leveling or slight decrease since then. Zn values increase to the present in unacidified lakes, but net deposition decreases in acidified (ph $<\tilde{\sim}$5.5) lakes.

These trends are spatially and temporally related to the consumption of fossil fuels and secondarily (perhaps) to smelting, gasoline-derived emissions, and other factors.

Pb from the atmosphere appears to be conserved approximately at the site of deposition. In the northeastern United States, present loading ranges from about 1 to possibly 6 $\mu g/cm^2/yr$, depending on position in the pollution gradient precipitation amounts, and vegetation type. The latter affects impaction and dryfall fluxes.

Although Zn concentration in precipitation generally exceeds Pb, Zn is not conserved by ecosystems. Retention varies inversely with the acidity of the system. Cu behaves similarly. Cu and Zn may have reached a steady state, with increased loading balanced by increased leaching.

All of these effects started about 100 years ago and have increased steadily to the present time. There is a suggestion that loading of Pb has leveled off, but accumulation continues. In areas receiving rain with pH < 5, Zn and Cu loading is apparently still increasing, but accumulation is near to or less than zero. Based on these data, it is clear that evaluation of the spatial and

temporal trends for atmospheric deposition of metals is needed to refine the conclusions reached by these surrogate rain collectors.

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